

Solutions for addressing specific LC-MS problematic pesticide residues in multiresidue methods. Part II

Online videotutorial

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Amadeo R. Fernández-Alba**



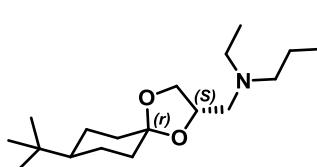
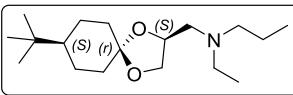
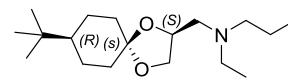
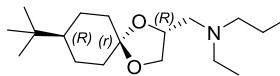
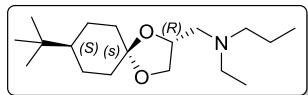
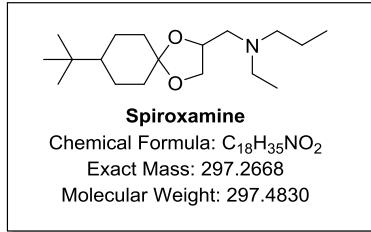
European Union Reference Laboratory for Pesticide Residues in Fruits & Vegetables

Tutorial length = 15 min

Problems derived from degradation processes in pesticides occurring prior to their analysis



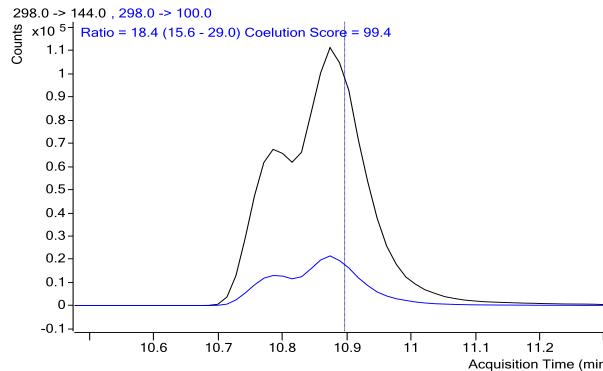
Degradation - Spiroxamine



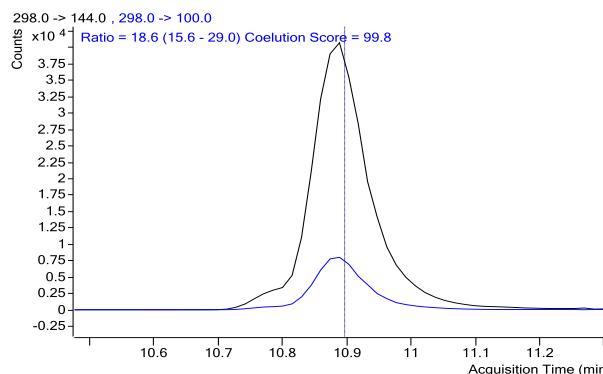
Cis diastereomer
(equatorial/axial)

Trans diastereomer
(equatorial/equatorial)

1.1E5



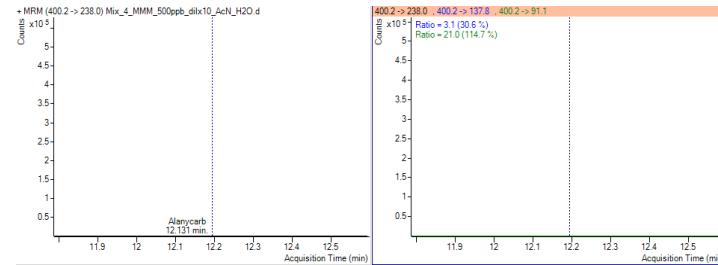
4.0E4



Degradation – (into) Methomyl

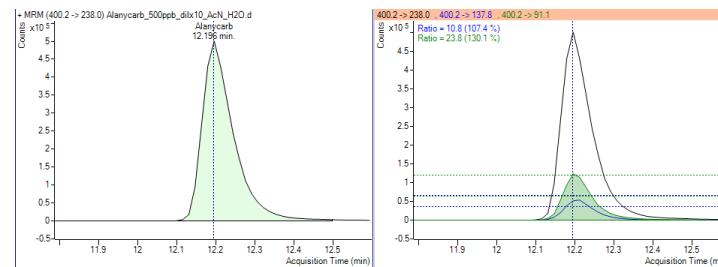
Alanycarb

(Mix – 10 mg/L in acetonitrile)



Alanycarb

(Stock solution – 10 mg/L in acetonitrile)

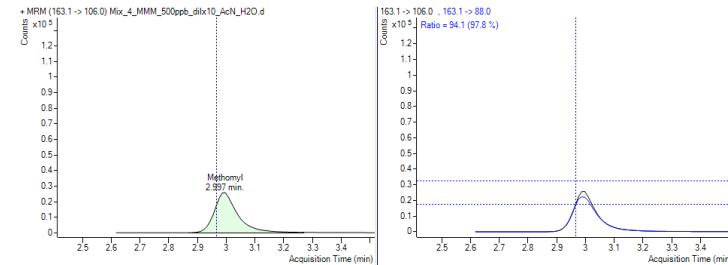


EURL

Degradation – (into) Methomyl

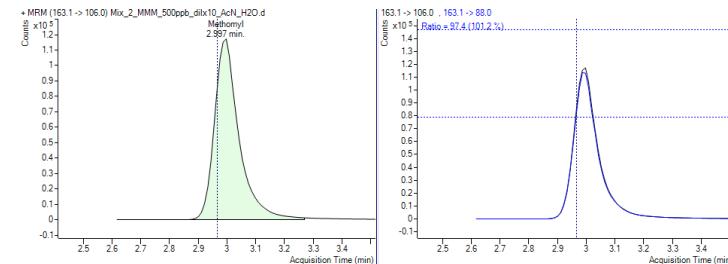
Methomyl

(Mix 4 – 20 mg/L in acetonitrile)



Methomyl

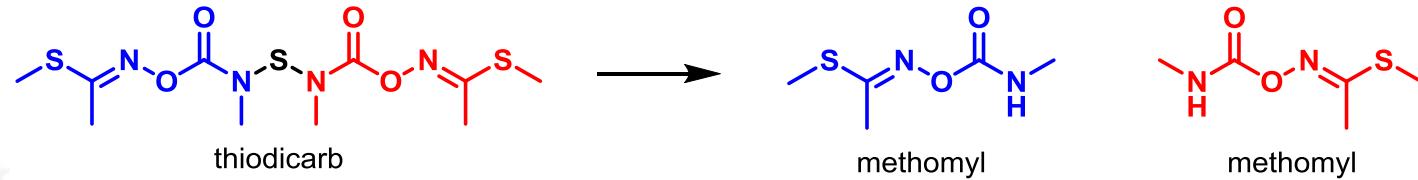
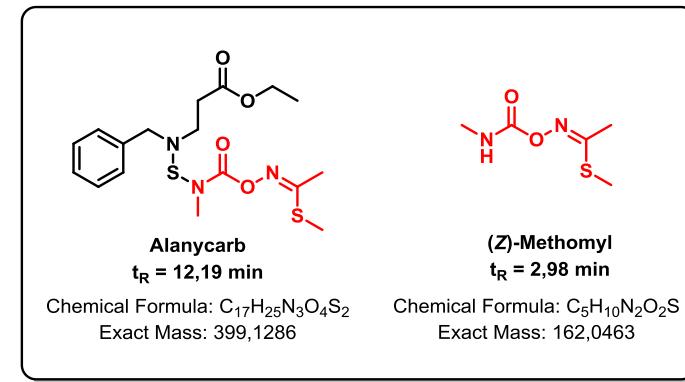
(Mix 2 – 10 mg/L in acetonitrile)



2.1 ppm of
methomyl in
mix 4?



Degradation - Methomyl



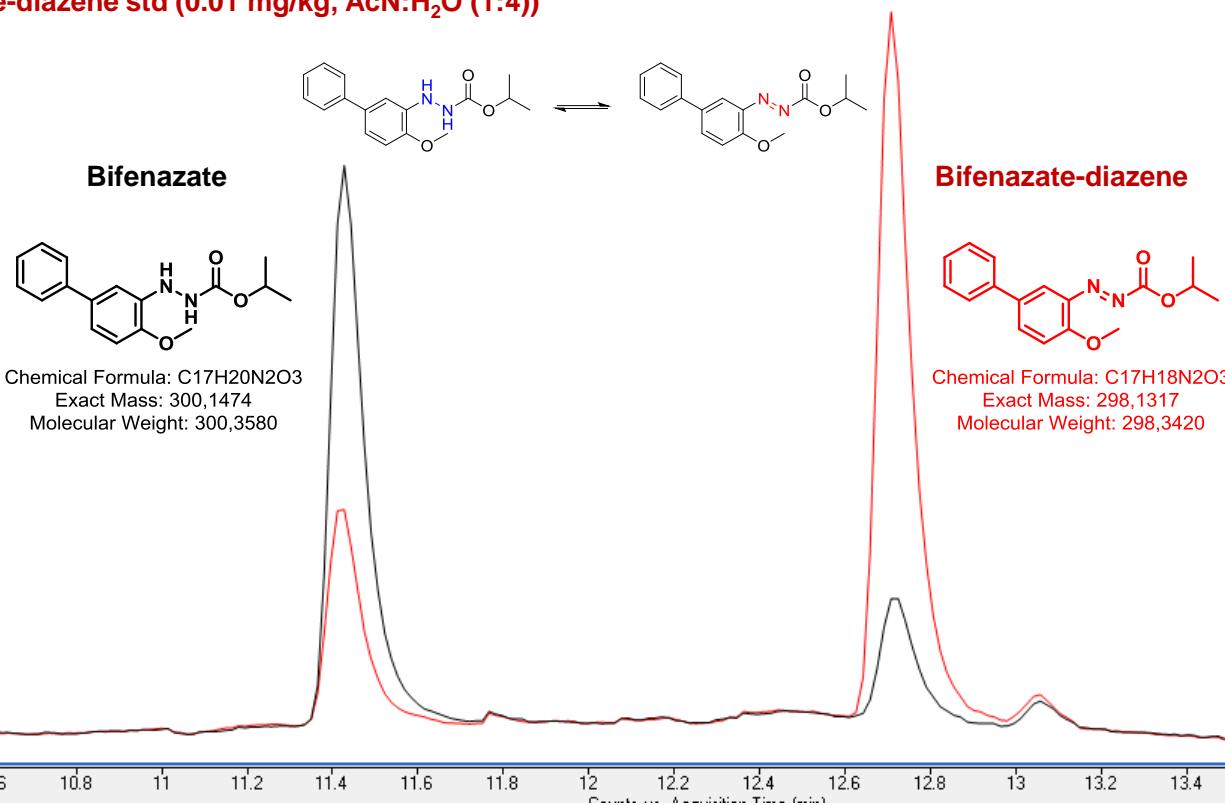
Compounds prone to interconversion processes during analysis



Interconversion - bifenazate

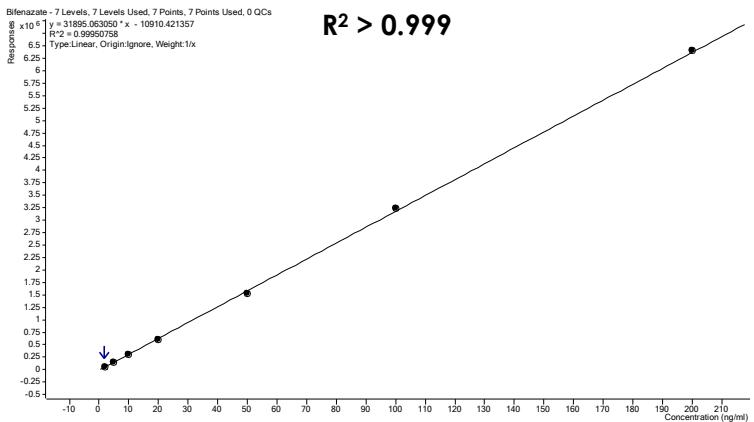
Black: bifenazate std (0.01 mg/kg, AcN:H₂O (1:4))

Red: bifenazate-diazene std (0.01 mg/kg, AcN:H₂O (1:4))

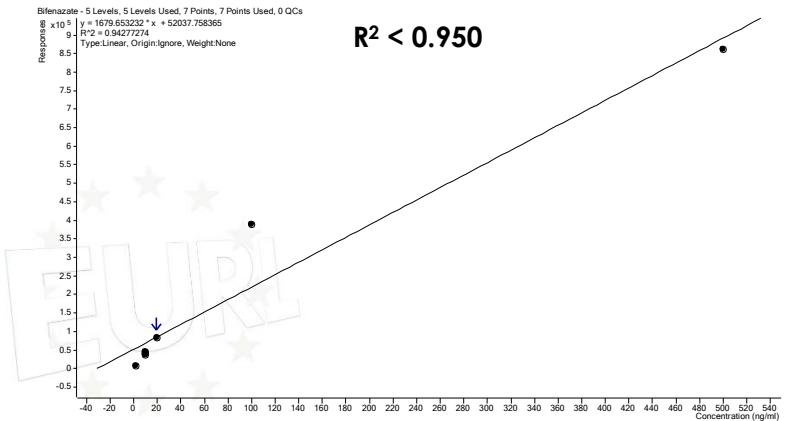


Interconversion - bifenazate

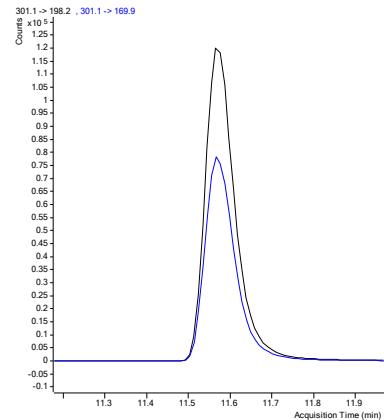
With L-ascorbic acid



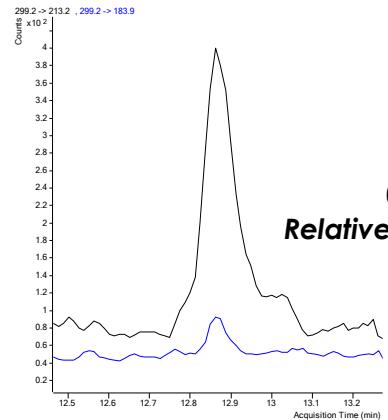
Without L-ascorbic acid



Bifenazate



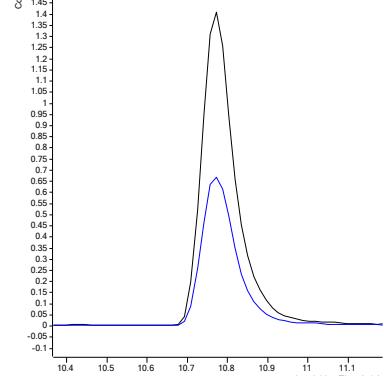
Bifenazate-diazene



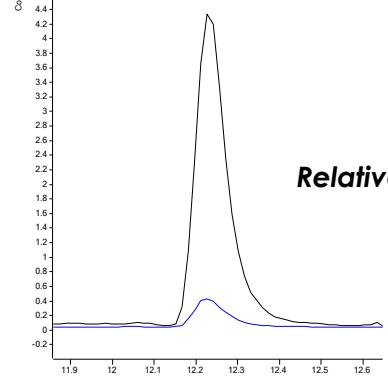
0.3 %

Relative abundance

301.1 -> 198.2 , 301.1 -> 169.9
Counts x10^-4



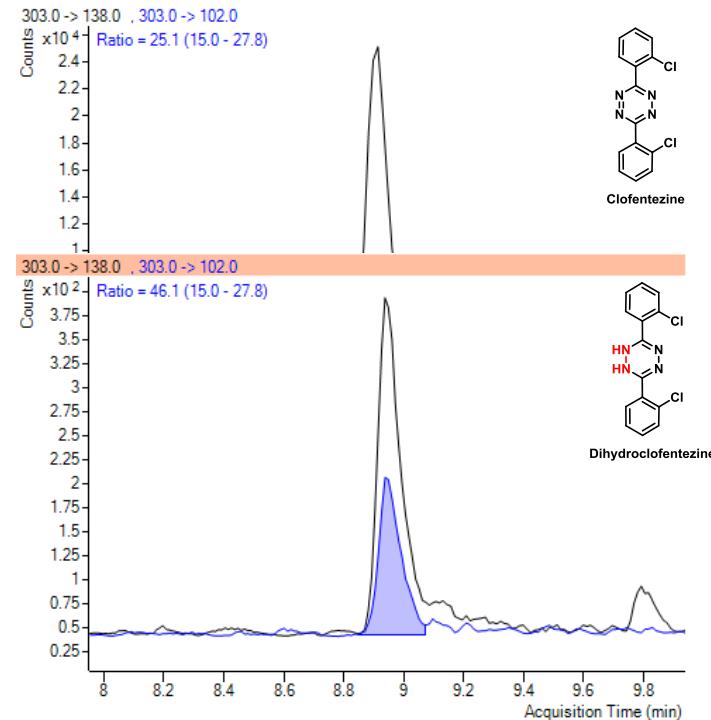
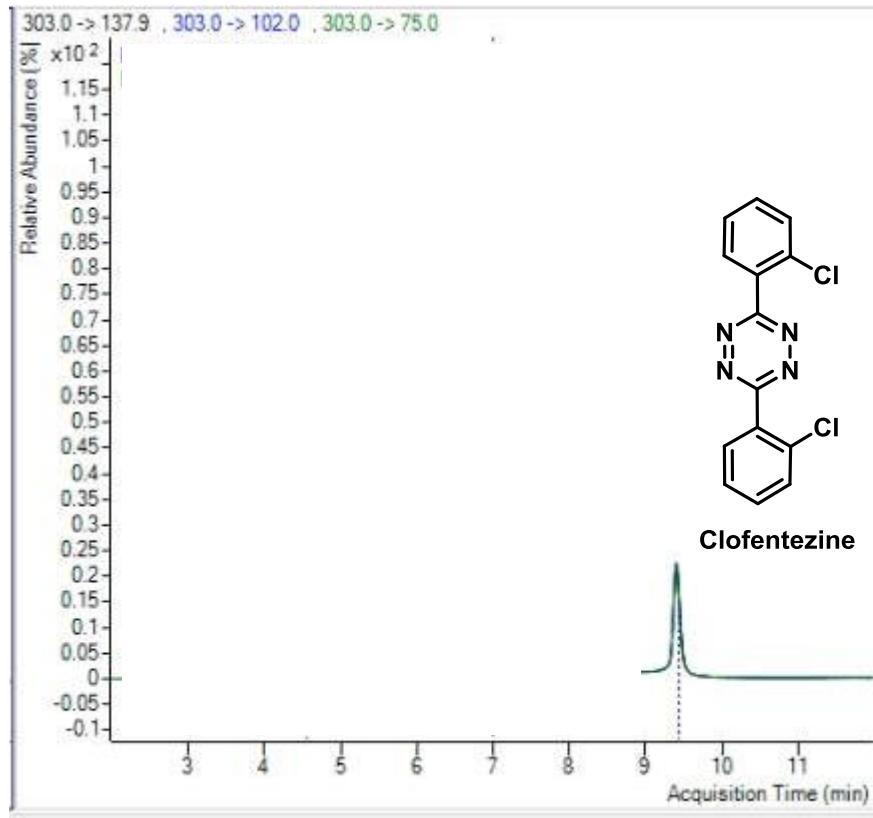
299.2 -> 213.2 , 299.2 -> 183.9
Counts x10^-3



28.1 %

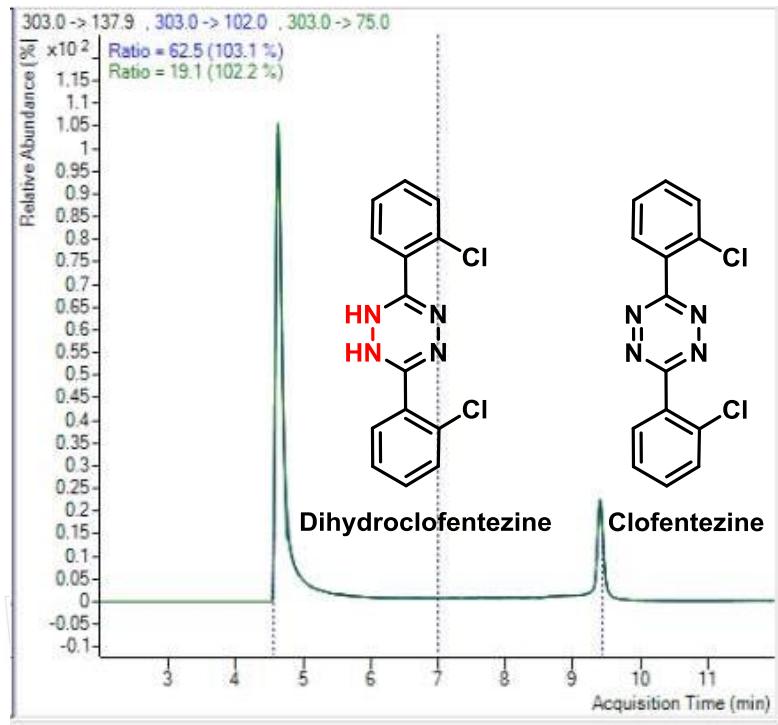
Relative abundance

Interconversion - Clofentezine

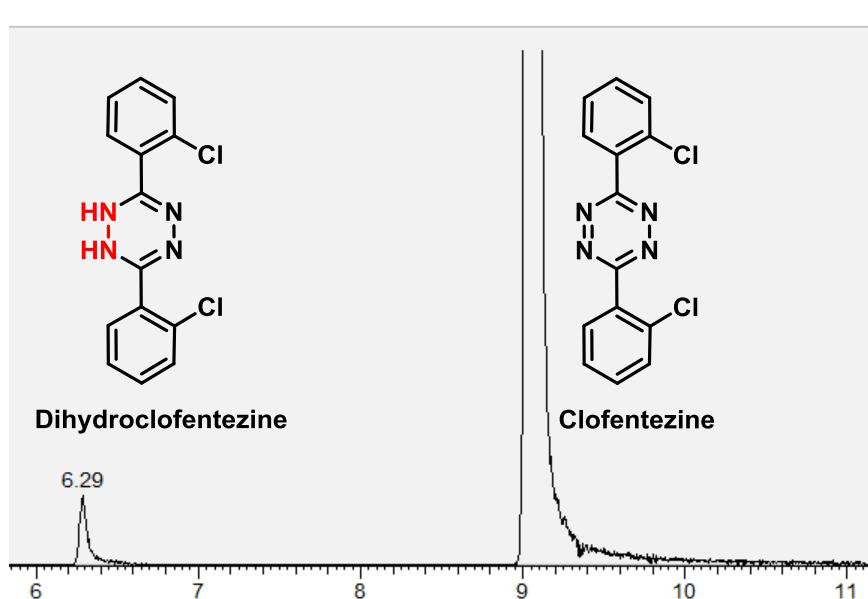


Interconversion - Clofentezine

High percentage of formic acid in the mobile fase
and/or little to no ammonium formate



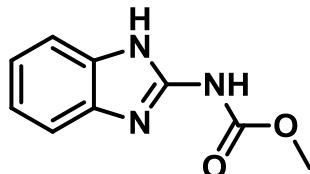
Low percentage of formic acid in the mobile fase
and/or ammonium formate



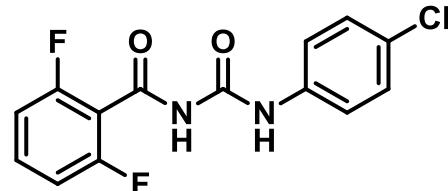
Solubility issues of certain LC-amenable compounds to consider for stock solution preparation



Solubility



Carbendazim



Diflubenzuron

Solubility

Insoluble in acetonitrile

Soluble in acidic methanol (HCl 2N)

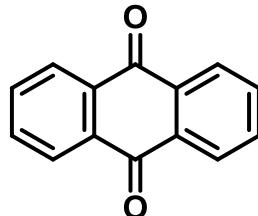
Ratio: 10 mg, 7 mL methanol and 0.1 mL
HCl 2 M

Solubility

Sparsely soluble in acetonitrile y
methanol (particularly troublesome in
acetonitrile)

Soluble in acetone

Solubility

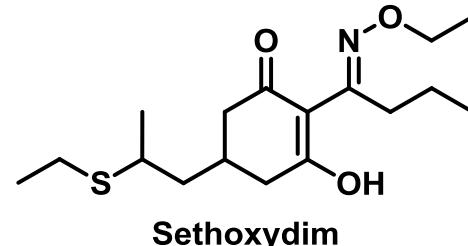


Anthraquinone

Solubility

Soluble in acetone or concentrated sulphuric acid

Alternatively, acetonitrile:acetone (93:7, V/V) and 10 min ultrasonic agitation at 35 °C (up to 500 ppm)



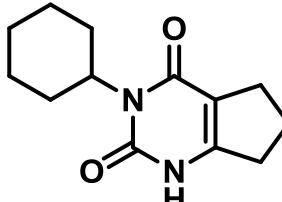
Sethoxydim

Solubility

Insoluble in acetonitrile, methanol, or water (neither with acidification)

Soluble in acetone (1000 ppm)

Solubility

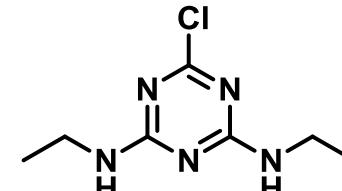


Lenacil

Solubility

Sparsely soluble in acetonitrile

Stock solution should be made using methanol and it is recommended ultrasonic agitation for 5 min prior to use



Simazine

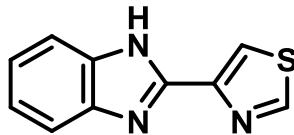
Solubility

Sparsely soluble in common solvents

Soluble in acetonitrile:acetone:DMSO (87:7:6, V/V/V) with the addition of HCl 2 M and ultrasonic agitation for 5 min

Prone to degradation

Solubility



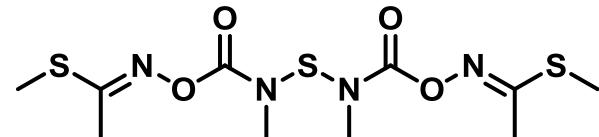
Thiabendazole

Solubility

Sparsely soluble in acetonitrile

Soluble in methanol or acetone

EURL



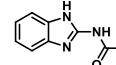
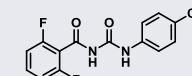
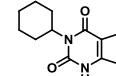
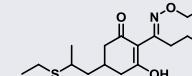
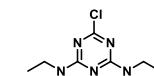
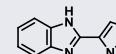
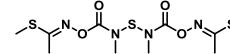
Thiodicarb

Solubility

Sparsely soluble in acetonitrile

To 5 mg, add 2 mL acetone, ultrasonic agitation for 5 min
Then, add an additional 2 mL acetone

Prone to degradation

Compound	Structure	Solvent	Comments
Anthraquinone		Acetonitrile:acetone (93:7, V/V)	5 min US (35 °C) ~500 ppm
Carbendazim		Methanol	HCl 2 M (1.5 %, V/V)
Diflubenzuron		Acetone	-
Lenacil		Methanol	5 min US prior to use
Sethoxydim		Acetone	-
Simazine		Acetonitrile:acetone: DMSO (87:7:6, V/V/V)	HCl 2 M (5.5 %, V/V)
Thiabendazole		Methanol or acetone	-
Thiodicarb		Acetone	5 min US

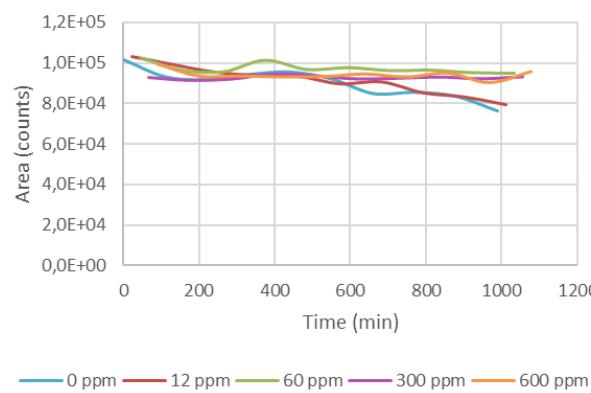
Use of L-ascorbic acid to stabilise labile analytes

Evaluation of 288 LC-amenable compounds

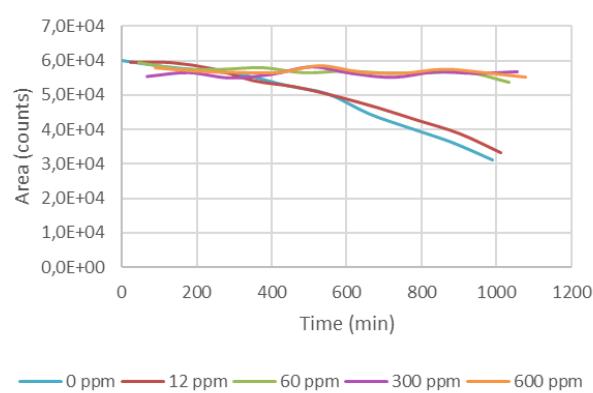


L-Ascorbic acid at different concentrations for LC injection vials preventing degradation

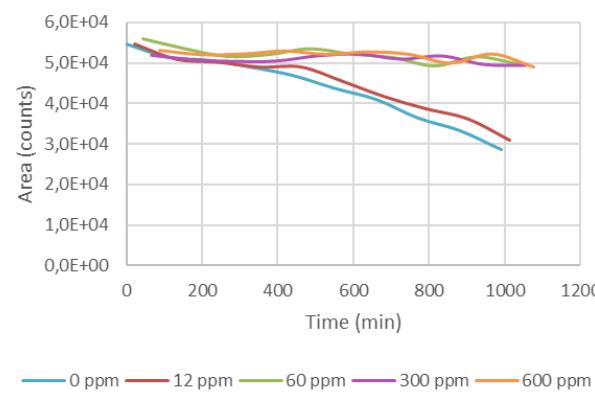
Bendiocarb



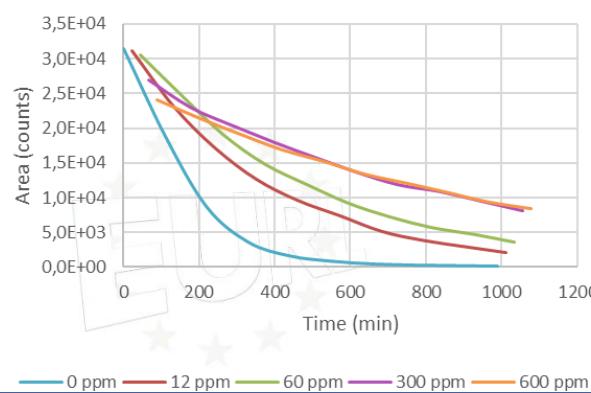
Trichlorfon



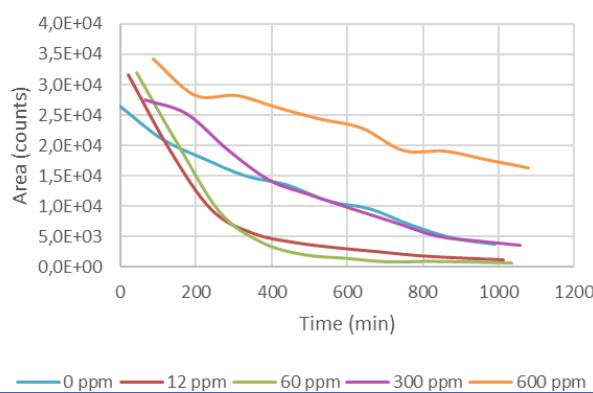
Cymoxanil



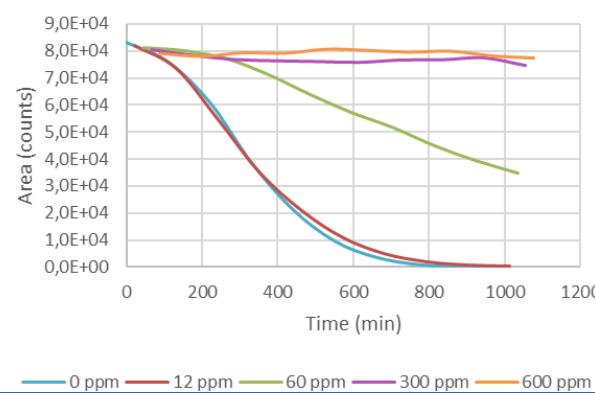
Dazomet



Dithianon

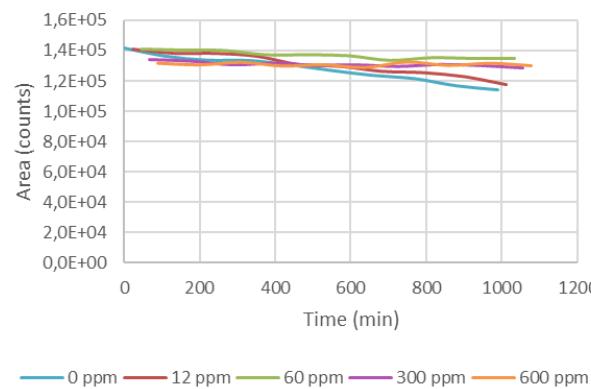


DMA

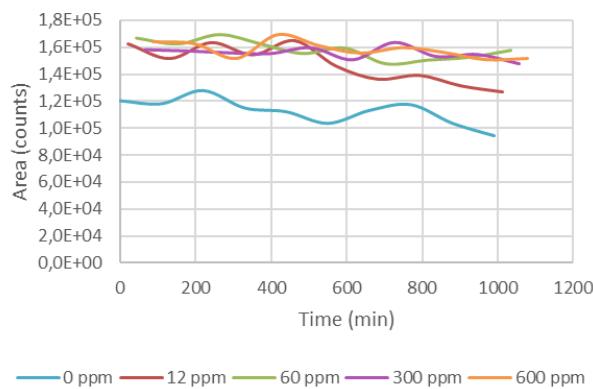


L-Ascorbic acid at different concentrations for LC injection vials preventing degradation

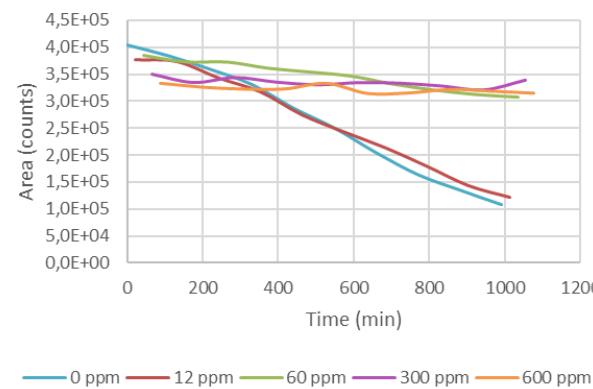
DMPF



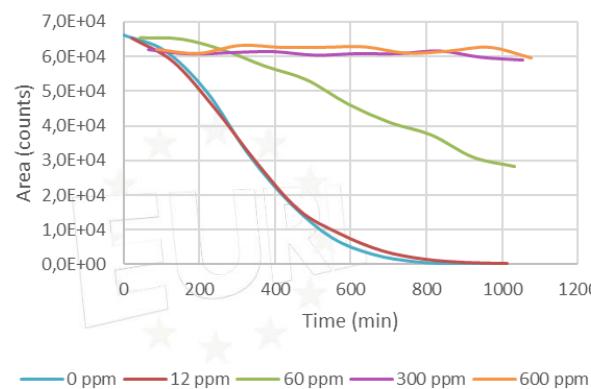
Fenpicoxamid



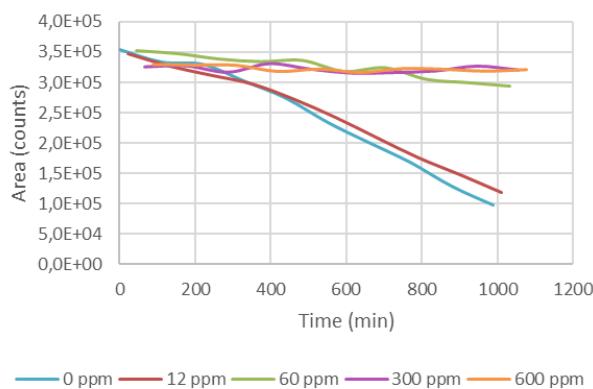
Formetanate



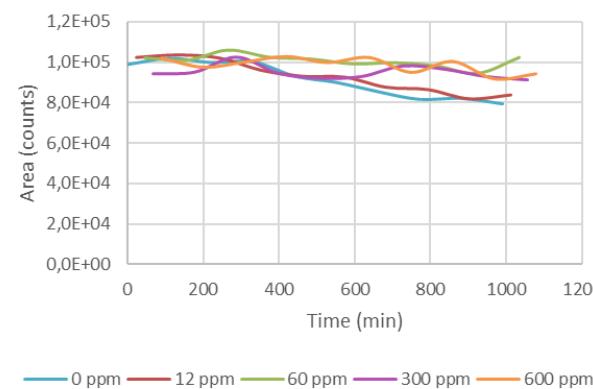
Methiocarb-sulfone



Methiocarb-sulfoxide

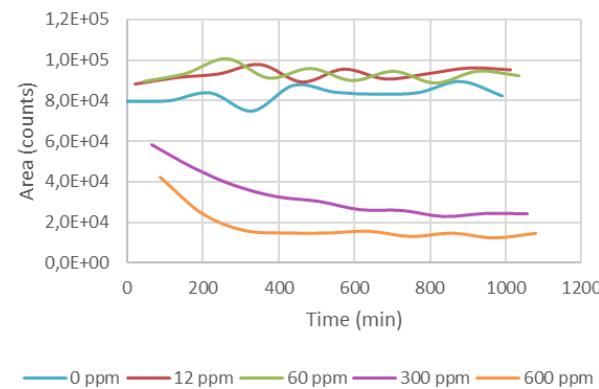


Phosmet

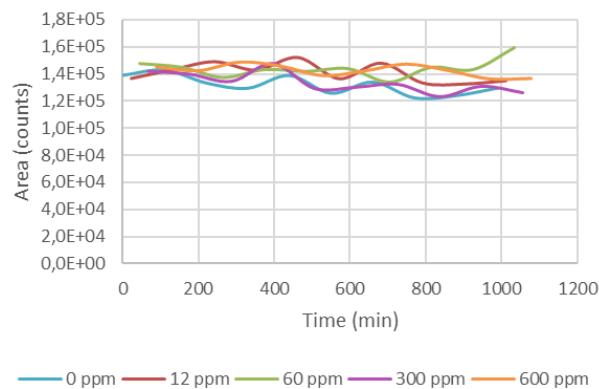


L-Ascorbic acid at different concentrations for LC injection vials preventing degradation

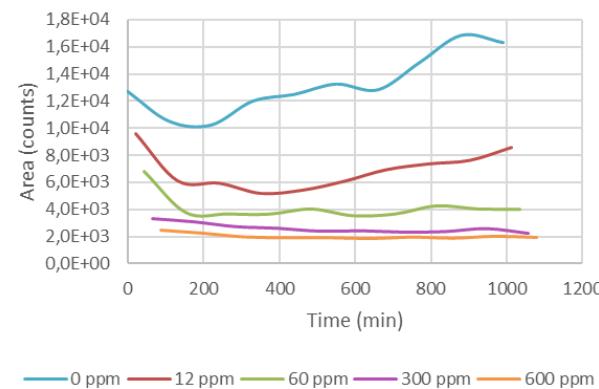
Clofentezine



Bifenazate

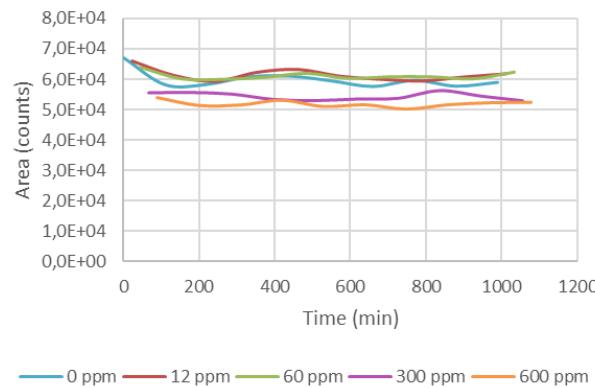


Bifenazate-diazene

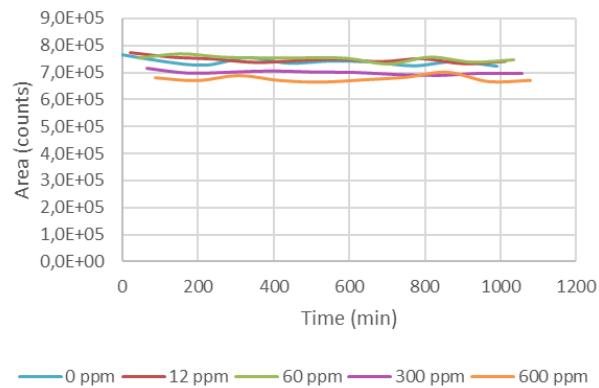


L-Ascorbic acid for LC injection vials and reduced instrumental response

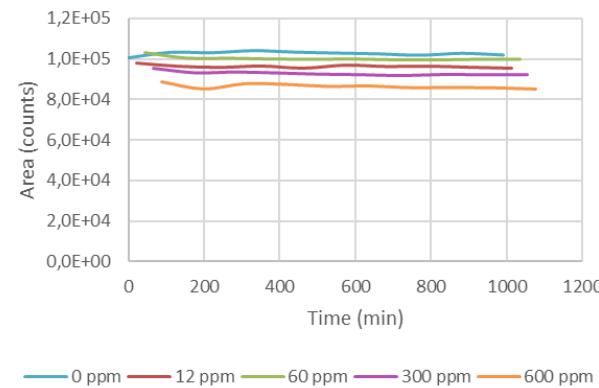
Butoxycarboxim



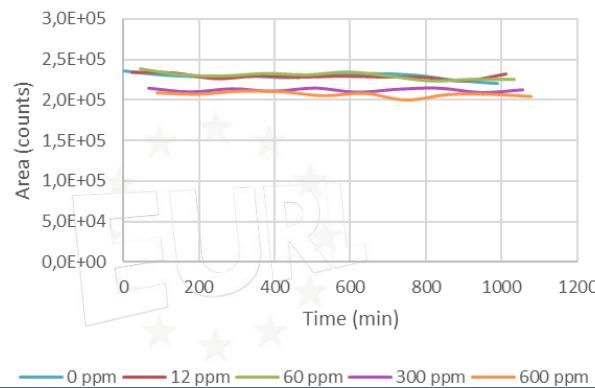
Carbendazim



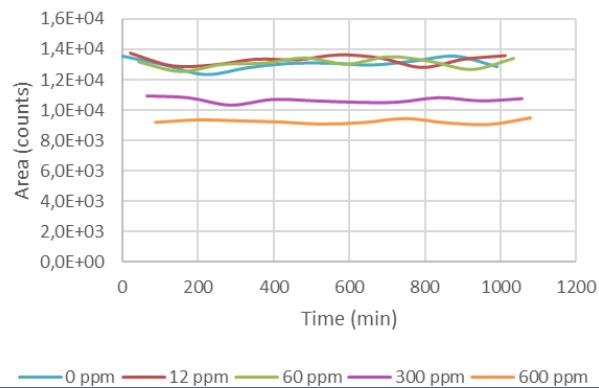
Cyromazine



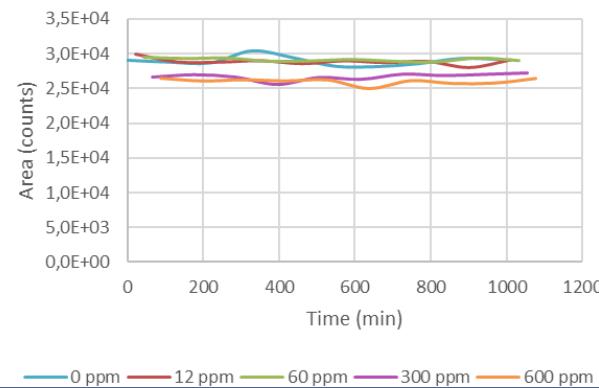
Demeton-S-methylsulfoxide



Flonicamid

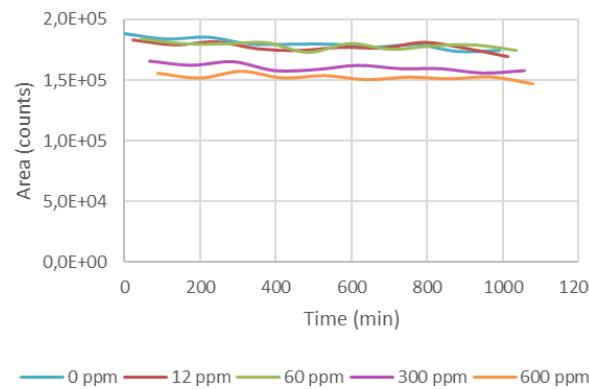


Methomyl

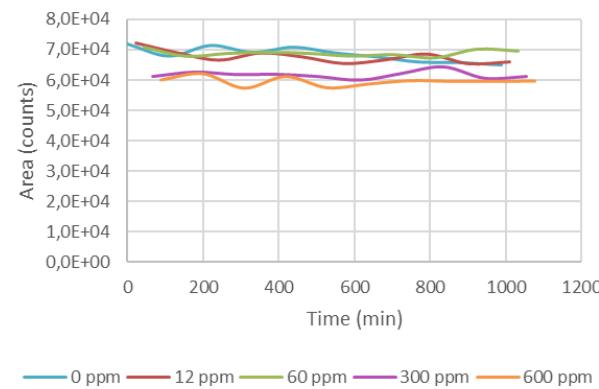


L-Ascorbic acid for LC injection vials and reduced instrumental response

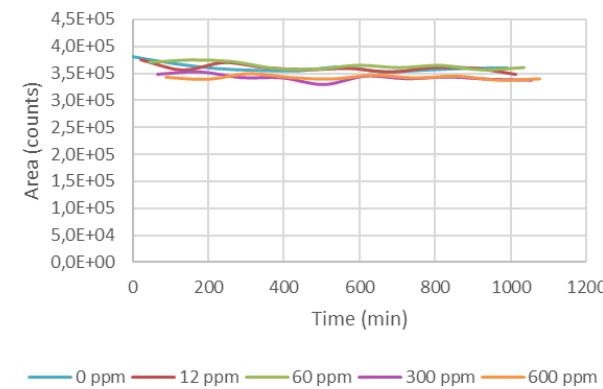
Omethoate



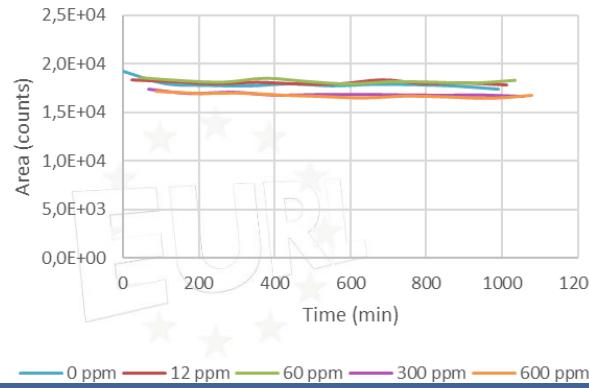
Oxamyl



Pirimicarb



Pirimicarb-desmethyl



Thank you for your attention

This online tutorial is part of a series of online tutorials that will continue through the rest of the year:

<https://www.eurl-pesticides.eu/docs/public/home.asp?LabID=500&Lang=EN>

